

# The Oil DROP



The U.S. EPA's Oil Spill Program Internal Report Vol. 3 No. 1 October 1999

#### **EPA Panel Warns Against Gasoline Additive**

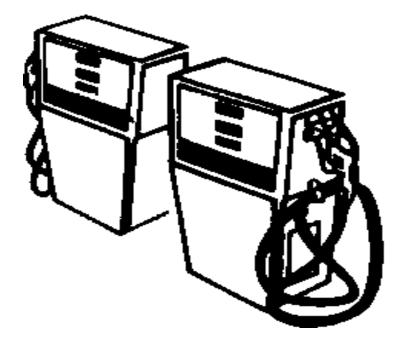
Methyl tertiary butyl ether (MTBE) is a chemical added to automotive gasoline to reduce tailpipe emissions of ground-level ozone. Unlike stratospheric ozone, which protects the earth from harmful ultraviolet light rays, ground-level ozone is an air pollutant that is regulated by EPA. EPA requires areas of the country with severe ozone pollution to use "reformulated" or "oxygenated" gasoline to help cut ozone levels in these areas. The primary additive used in reformulated gasoline is MTBE. MTBE is a member of a class of chemical compounds, ethers, whose unique properties are enhanced solubility in water and chemical attraction to water molecules. The use of MTBE has increased dramatically since 1992. It is used in about a third of the nation's motor fuel in 16 states. Some areas of the country are using MTBE only in the winter months; other areas are required to use it year round.

MTBE once was touted as key to cutting air pollution from automobiles. However, an EPA advisory panel found that, although reformulated gasoline has contributed to significant air quality improvements, MTBE poses a growing threat to drinking water. Federal research has shown that MTBE causes tumors to grow in rats and may be a human carcinogen as well. A study done in California has shown that 10,000 of the state's

groundwater sites are affected by MTBE.

The advisory panel comprises diverse interests from environmentalists to oil industry executives and state regulators. The panel found that MTBE molecules travel unusually fast through soil and into groundwater once gasoline is released into the environment. MTBE can be released in gasoline spills and through leaks in underground storage tanks (USTs). Each year, nine million gallons of gasoline (the equivalent of a full supertanker) are spilled in the United States from leaks, inefficient engines, and carelessness, according to the Alliance for Proper Gasoline Handling.

A summary of the panel's report indicates that the panel found evidence that trace levels of MTBE are present in 5 to 10 percent of the drinking water in parts of the country that use oxygenated gasoline. Although the levels found so far are not believed to pose a risk to human health, the panel took them as a warning that widespread use of MTBE could pose a future threat. Thus the panel concluded that MTBE use in reformulated gasoline "should be reduced substantially." Two panel members recommended it be banned entirely. For now, EPA and the MTBE industry hope that current EPA UST regulations protect the public from MTBE groundwater contamination. However, the industry standards referenced in



these regulations may be flawed, allowing MTBE to escape from tanks and piping while containing gasoline, say manufacturers of piping and tanks used in more than 50 percent of all retail motor fuel facilities.

**EPA Administrator Carol Browner** said "EPA must begin to significantly reduce the use of MTBE in gasoline as quickly as possible without sacrificing the gains we've made in achieving cleaner air." EPA will ask Congress to develop new legislation designed to maintain the reformulated gas program that has been credited with cutting air pollution from cars, but with an aim toward phasing out MTBE use to protect water supplies. EPA staff have met with representatives of Underwriters Laboratory (UL) and have asked to be included in the industry advisory

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group for the UL standards related to underground storage tanks.

Implications of MTBE issues for oil spill planning prevention and response will be discussed at the upcoming Fuels Management Workshop sponsored by EPA Region 10 and the State of California, and at EPA's March 2000 Freshwater Spills Symposium.

#### Fatty Acids from Trees and Beans

Fatty acids are a group of non-petroleum oils commonly used as additives in industrial lubricants, metalworking fluids, and greases. Fatty acids are made up of carbon chains with double bonds. Although we may not think of trees and beans as being oily, wood pulp and castor bean oils are among the richest sources of fatty acids, and they both have chemical properties that make them desirable in industrial applications.

Fatty acids from wood pulp come from tall oils, a by-product of the paper-making industry. In the papermaking process, wood fibers are separated from other substances. The fibers become the pulp that is turned into paper, and most of the remaining substances form what is called "black liquor." Tall oils can be separated from black liquor and further refined into fatty acids. In addition to their primary product, most of the large paper companies in the United States also produce tall oils and fatty acids. The two largest paper producers have a total of 23 facilities that produce tall oils or tall oil products.

Vegetable oils, like castor oil, are also a large source of fatty acids. Eighty percent of the world's castor oil is produced in India. One of the most common castor oil products is sebaic acid. It is often used in waterbased metalworking fluids because it keeps the water in the fluid from coming into contact with metal, which helps prevent corrosion.

Like other non-petroleum oils, tall oils, castor oils, and fatty acid products can have the same harmful effects as petroleum oils and are subject to oil spill prevention regulations. Spills of non-petroleum oils can coat animals' fur and feathers causing suffocation, starvation, and freezing; they can cause oxygen depletion in water leading to fish kills; and they can contaminate drinking water supplies. These oils can also foul shorelines and recreational areas, and as they degrade they can produce rancid odors. Thus, spill prevention and response are still very important concerns.

## Alaska Pipeline Lease Expiration Prompts Environmental Study

A 30-year lease of federal lands occupied by the Trans-Alaska Pipeline will expire in 2004, prompting a rigorous environmental review. The pipeline covers a distance of 800 miles between Prudhoe Bay and Valdez through public land. The seven oil companies that own the pipeline-Amerada Hess, Arco, BP Amoco, Exxon, Mobil, Phillips, and Unocalcurrently lease the public lands from the United States and the State of Alaska. Regulation of the pipeline is the responsibility of the state-federal Joint Pipeline Office. The federal

Bureau of Land Management (BLM) will receive the lease renewal application from the oil companies.

Federal law requires that environmental effects of any significant federal decision be studied prior to implementation. An environmental assessment is typically performed to meet this requirement. Due to the magnitude and high profile of the pipeline study, federal officials are planning an in-depth environmental impact statement (EIS) for the renewal examination. The EIS is likely to be time and cost intensive and may be contracted to a private firm and overseen by the BLM. Most of the work will be funded by the oil companies.

The EIS will provide government officials with detailed information regarding the pipeline's effects on natural resources, wildlife, and people that share space with it. Operation and maintenance of the pipeline has been problematic in the past and is likely to be a main topic of the EIS. The issues covered by the statement will ultimately be decided through a series of public meetings that will begin after the companies

#### **Quick Facts on the Trans Alaska Pipeline System**

The Trans Alaska Pipeline System was first put into operation on June 20, 1977. Almost half of the pipeline is above ground to prevent permafrost thaw. The pipeline is designed to move 20 feet side to side and 5 feet up and down because of seismic activity in the area. Other interesting facts include:

Area covered: 16.3 mi<sup>2</sup> Diameter: 48"

Length: 800.302 mi

Throughput (ave): 1.46 mil bbl/day

Cost: \$8 billion

Minumum Height: 5 ft. Animal Crossing height: 10 ft. Pipeline Bridges: 13 Min. Temperature: -80°F

Employees: 925

submit an application to renew the lease.

Findings of the EIS may lead to changes in the details of the lease agreement, which covers items ranging from spill response to erosion control. BP Amoco has stated that it believes pipeline impacts on the Alaskan environment have been minimal and expects that view to be reinforced by the EIS. Alaska has its own lease agreement with the oil companies, also expiring in 2004, and will perform its own assessment. However, the state plans to work closely with federal officials in the development of its review.

#### Slow Recovery After Exxon Valdez Oil Spill

A report issued in February 1999 by the Exxon Valdez Oil Spill Trustee Council suggests that recovery from the spill is slow and that spilled oil continues to impact the environment in Prince William Sound. The Council consists of three state and three federal representatives (trustees or their designates) assembled to administer restoration funds and restore resources and services damaged by the spill. Approximately 11 million gallons of oil released into the Sound on March 24, 1989, impacted wild and plant life along 1.300 miles of shoreline.

A report released by the Council in February this year states that only two species affected by the spill have fully recovered. Exxon (the company responsible for the spill) made conflicting statements on the tenth anniversary of the spill, claiming that most of the multitude of species in the Sound were either never effected by the spill or have fully recovered and they and the environment are "healthy and robust." Council findings are at odds with Exxon's





recovery portrayal showing that 8 of 24 species suffering population decreases or sublethal effects attributable to the spill are showing no indication of recovery.

Scientific studies performed for the Council contradict the hypothesis that the oil's toxicity would quickly diminish as the oil weathers in the environment. Even very small amounts of remaining oil are highly toxic according to the Council. Laboratory results have found that levels at only 1 part per billion have effects on organisms such as herring and salmon eggs. As storms and natural processes constantly stir up shorelines, the potential for leaching of remnant oil from isolated deposits increases, as does the potential for detrimental effects on endemic species. Species that spawn in, feed in, or frequent the intertidal zone, such as mussels, sea otters, and ducks, are particularly at risk.

Exxon claims that other "background" levels of petroleum in the water due to human activity, such as fishing and shipping, are just as likely to produce such effects. Additionally, they have stated that the Council is making the assumption that changes observed in species is linked to the oil spill.

Other factors, such as ocean temperature increases, predator-prey relationships, fishing, and habitat degradation can alter species' recovery environment. However, the Council has noted that the effects they have found appear to be occurring in areas which received oil and not in those untouched by the spill.

### Oil Spill Fingerprinting Using GC x GC Analysis

The United States Coast Guard (USCG) has tested a new method of chemical fingerprinting that shows promise for analyzing light petroleum compounds. Chemical fingerprinting uses chemical analysis to determine the make-up of spilled oil. If the source of a spill is not obvious, chemical fingerprinting can be used to identify the person or company responsible for the spill (responsible party). Clearly identifying a responsible party allows the government to recover the costs of cleaning up the spill and compensation for damages to natural resources.

Since the 1970s, analysis using infrared spectrometry and gas chromatography has been used to fingerprint oil spills. More recently, gas chromatography with mass spectrometry detection (GC/MS) and high-resolution capillary gas chromatography (HRGC) have provided more detailed fingerprints of spills. These methods cannot identify light hydrocarbons, however, because they have limited resolving power and require heavy compounds to make positive identifications.

In an attempt to find an improved identification method, comprehensive two-dimensional gas chromatography (GC x GC) was applied to a test oil spill case. GC x GC has been successfully used to separate many complex mixtures, including identification of pesticides in human blood serum. GC x GC has a very high resolving power and subjects the sample to two different separations, providing a much clearer picture of the components in the sample.

GC x GC analysis was applied to an oil spill case from the USCG's Marine Safety Laboratory. The spill was collected approximately 24 hours after an 150-gallon spill into saltwater. This spill sample was compared to samples collected from two suspect vessels in the area (Source 1 and Source 2).

Visual comparisons between the GC x GC chromatograms of the spill and the two suspect samples show small differences, especially in the heavy aromatic region. The aromatic region is useful for identifying oil samples because of the relationship between their chemical structure and how long it takes for the compounds to proceed through the chromatograph. Qualitative and quantitative results determined that Source 1 was the

## Oil Facts Common Uses of Petroleum Oils

When we think of products made from oil we usually think of fuels like gasoline and diesel, and lubricants such as motor oil. Chemicals derived from oil are used to make many other products as well. Many of these include plastics and pharmaceuticals. Some products that can be made from or contain oil-derived substances are listed below:

bandages asprin carpet denture adhesives floor wax cortisone dishwashing liquid panty hose upholstery rubber bands tires film car bodies bubble gum toothpaste life jackets quitar strings linoleum contact lenses crayons insulation fishing lures lipstick antihistamines cold cream candles ammonia artificial turf insect repellent lip balm glues/adhesives saccharine ink

probable source for the spill. This finding is consistent with HRGC and GC/MS analyses that were conducted by the USCG, demonstrating that GC x GC analysis works for oil spill fingerprinting.

Using the GC x GC method, lighter, more complex separations of petroleum products can be performed. GC x GC provides for an easier identification method because of its high resolving power. Future work with GC x GC may include analysis of weathered and biodegraded samples, comparison of different petroleum products, and direct comparison between GC x GC and GC/MS methods.

# Gasoline Spill Closes Ohio River

A barge collision on the Ohio River spilled 69,000 gallons of gasoline on August 9, 1999. Five barges were involved in the accident; a series of

four barges loaded with gasoline, which were being towed on the river, struck a docked barge containing cumene, a chemical used to make plastics. Gasoline was spilled from two barges; little or no cumene was released to the environment. The accident closed the river to commercial traffic for two days while recovery efforts were implemented.

The collision took place at a fleeting area on the river near Mount Vernon, Indiana. The Mount Vernon city water intake, located down river of the spill, was closed until the spill was cleaned up. The 7,000 people of Mount Vernon rely on the Ohio River for most of their potable water.

Booms were deployed to contain the spill. Work crews completed operations by August 10 and river traffic was restored. The cause of the accident is still under investigation.

The barges carrying the gasoline are owned by Waxler Towing; the barge containing the cumene is owned by Marathon Ashland Petroleum, LLC.

# Oil Spill News from the Americas

#### Pipeline Breach in Brazil

On August 1, 1999, a pipeline breach in the Buracica field near the cattle farming town of Catú, Brazil, released as much as 180,000 gallons of crude oil, according to the Bahia Oil Workers union. The pipeline is owned by Petrobrás, Brazil's stateowned oil company. According to company reports, as little as 11,000 was released.

The spill reached pasture areas of several nearby farms. Owners of two farms were forced to move cattle away from affected fields. Petrobrás assumed responsibility for feeding displaced animals for 30 days; the amount of time estimated to complete removal and cleanup operations on the impacted land.

## Spills in the Amazon Threaten Wildlife

A report published by the Brazilian Navy Ministry in June stated that the large number of oil spills in the Amazon River and its tributaries in the past five years is threatening the region's flora and fauna. The report stated that in the past five years, 35 spills have been recorded in rivers totaling approximately 245,000 gallons. The number of oil spills per year are increasing; there were 5 spills reported in 1994 and 13 in 1998. Most of the spills have impacted the Madeira River, the third largest in Brazil. The Madeira River is known for its diverse fish and plant populations. Although 18 responsible parties have been identified, the report states a single shipping company, Navezon Linhas

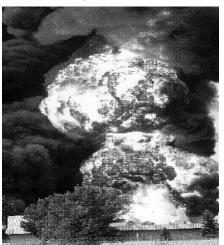
da Amazônia, is responsible for one third of the spills. The company has been fined 11 times.

## Canadian Oil Facility Explodes

A fire and series of explosions at the Hub Oil recycling plant in Calgary, Alberta killed two workers and injured five others August 9. Smoke generated by the fire caused evacuation of approximately 250 residents from nearby areas. An additional 1,000 residents were advised to stay indoors and keep their windows and doors closed to avoid contact with the noxious smoke.

Fire department and emergency officials stated that up to 20 separate explosions shook the site, beginning around 11:30 a.m. and continuing through the afternoon. The fire was believed to have started in an oil storage tank, then moved from tank to tank, sparking the string of explosions. Firefighters were not able to safely enter the site until after 8:30 p.m.; the fire was brought under control by 11 p.m. The intensity of the blaze forced firefighters to abort an early attempt to control the inferno: an aerial truck was abandoned and consumed by the fire.

The one-acre site occupied one city block in Calgary. Hub Oil used the



**Top Ten Oil Producing and Consuming Countries** 

Rank	Top Producers	Million barrels/day	Top Consumers	Million barrels/day
1	Former Soviet Union	11.5	United States	16.2
2	United States	7.2	Former Soviet Union	8.1
3	Saudi Arabia	6.2	Japan	5.3
4	Iran	3.1	Germany	2.7
5	China	2.8	China	2.3
6	Mexico	2.7	Italy	1.9
7	Venezuela	2.1	France	1.9
8	Iraq	2.1	United Kingdom	1.7
9	United Kingdom	1.9	Canada	1.6
10	Nigeria	1.8	Spain	1.0

Source: Educational Technology Review Center, 1997.

plant to consolidate used motor oil from local automotive repair shops for recycling. In addition to oil, the facility also stored diesel, jet fuel, propane, and sulfuric acid.

#### Ro-Clean Desmi Introduces New Skimmer

The following announcement does not constitute EPA endorsement or EPA approval of the product described. It is intended only to notify the response community of newly available equipment.

Ro-Clean Desmi has introduced a new disc skimmer for recovering floating oils. The new Ro-Disc is a high efficiency skimmer for inland waters, and industrial process applications such as separators and tanks. The Ro-Disc is designed for use in high concentrations of light and medium oils. The company claims that the skimmer can recover oils at a rate of up to nine gallons per minute.

The skimmer uses a single bank of rotating oleophilic (oil attracting) discs driven by a hydraulic motor. Oil is recovered from the water surface as it adheres to the disc surface. As the discs are rotated through the skimmer head, oil is scraped off and collected in the sump on a continuous basis. Disc speed can be varied to optimize efficiency according to conditions.

Skimmed oil is removed by a hydraulically driven peristaltic pump, which can run dry and will self-prime.

For more information, see the company's web site at www.ro-cleandesmi.com.